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## (54) EL FLUORESCENT MATERIAL POWDER

## (57)Abstract:

**PURPOSE:** To obtain the powder comprising zinc sulfide as a matrix material, and an activating agent and a coactivating agent which are used as light-emitting centers, having the characteristics of high brightness and long life, and useful for flat face type displays, luminous panels for display, etc.

**CONSTITUTION:** This fluorescent material powder comprises (A) zinc sulfide as a matrix material, (B) an activating agent (preferably the ion of at least one kind of element selected from copper, manganese, silver, gold and rare earth elements, especially preferably copper ion), and (C) a coactivating agent (preferably the ion of at least one kind of element selected from chlorine, bromine, iodine, and Al, especially preferably chloride ion). The fluorescent material powder uniformly has flat lamination defects in a high density over the whole body of the particle wherein the average face distance of the lamination defects is 0.2-10nm, and preferably further has an average particle diameter of  $25\mu\text{m}$ .

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**CLAIMS**

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[Claim(s)]

[Claim 1] (Electroluminescence EL) fluorescent substance powder which is fluorescent substance powder which uses zinc sulfide as a parent and contains an activator and co-activating agent, has the field-like stacking fault to the whole particle at homogeneity and high density, and is characterized by the average spacing of the stacking fault being 0.2-10nm.

[Claim 2] The mean particle diameter of fluorescent substance powder is 25 micrometers. EL material powder of following claims 1.

[Claim 3] EL material powder of claims 1 or 2 whose activators are a kind of ion chosen from copper, manganese, silver, gold, and rare earth elements at least.

[Claim 4] EL material powder according to claim 1 to 3 whose co-activating agent is a kind of ion chosen from chlorine, a bromine, iodine, and aluminum at least.

[Claim 5] EL material powder according to claim 1 to 4 whose activator is a copper ion and whose co-activating agent is a chloride ion.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[Industrial Application] This invention relates to the fluorescent substance powder containing the activator and co-activating agent which use zinc sulfide as a parent and take the lead in luminescence, and an electroluminescence (EL) fluorescent substance especially long lasting by high brightness.

#### [0002]

[Description of the Prior Art] EL material is a fluorescent substance of an electrical-potential-difference excitation mold, and the distributed process input output equipment EL and the thin film mold EL which were used as the light emitting device on both sides of fluorescent substance powder between electrodes are known. The general configuration of distributed EL material consists of structure to which at least one side put what distributed fluorescent substance powder in the binder of a high dielectric constant between the transparent electrodes of two sheets, and emits light by impressing alternating current electric field between two electrodes. since it has many advantages — the light emitting device created using EL material powder can be considered as the thickness of several mm or less, and are a field emitter, and there is no generation of heat and luminous efficiency is good — luminescence panels for a display, such as a road sign, various interiors, and exterior ones — the application as the light source for flat-panel displays, such as lighting of business and a liquid crystal display, etc. is expected.

[0003] As EL material powder, that by which co-activating agent, such as activators (metal ion as an emission center), such as copper, and chlorine, was added is widely known by using zinc sulfide as a parent. However, the light emitting device created using this fluorescent substance powder has the fault that luminescence brightness is low and a luminescence life is short compared with the light emitting device based on other principles, and, for this reason, various amelioration has been tried from the former. For example, it anneals at 700–950 degrees C, or hot pressing is carried out to annealing and coincidence, JP,61–296085,A is transferred to cubic system, after manufacturing the medium fluorescent substance powder of hexagonal system and applying hydrostatic pressure to this under ordinary temperature by calcinating the mixture of zinc sulfide, a copper compound, and a halogenide at 1000–1200 degrees C, and the method of manufacturing high brightness and long lasting fluorescent substance powder is indicated. Moreover, to JP,6–33053,A, medium fluorescent substance powder is replaced with the approach of annealing in atmospheric air, atmospheric air is intercepted and re-calcinated under sulfate existence, and the manufacture approach further heat-treated comparatively at low temperature in atmospheric air after etching is indicated. Although the fluorescent substance powder manufactured by the latter approach has luminescence brightness higher than the conventional thing and the life also has the long advantage, the raise in brightness and reinforcement are called for further.

#### [0004]

[Problem(s) to be Solved by the Invention] This invention solves the above-mentioned technical problem in the conventional EL material powder, and aims at offering the EL material powder which has high brightness sufficient as an object for light emitting devices, and a long lasting property.

#### [0005]

[Means for Solving the Problem] It is thought that the core of EL luminescence of EL material powder is the interface part of the needle crystal, such as copper sulfide ( $\text{Cu}_2\text{S}$ ) of an activator, and the zinc sulfide parent which deposited in the stacking-fault section which exists in a particle ("copper activation fluorescent substance" ceramic 26 (1991) No.7). Since this invention person etc. used the stacking fault to which the conventional EL material powder exists automatically in a particle, the consistency of the

stacking fault which takes the lead in EL luminescence was low, therefore found out that high brightness luminescence could not be obtained. Then, in this invention, made the whole particle produce a field-like stacking fault in homogeneity and high density by applying impulse force to medium fluorescent substance powder etc., the whole zinc sulfide particle was made to distribute a part for the core of EL luminescence to homogeneity, and luminescence brightness and a luminescence life were substantially raised by raising the consistency.

[0006] That is, according to this invention, the EL material powder which has the following configurations, and its manufacture approach are offered.

- (1) EL material powder which is fluorescent substance powder which uses zinc sulfide as a parent and contains an activator and co-activating agent, has the field-like stacking fault to the whole particle at homogeneity and high density, and is characterized by the average spacing of the stacking fault being 0.2–10nm.
- (2) The mean particle diameter of fluorescent substance powder is 25 micrometers. The following above (1) EL material powder.
- (3) The above whose activator is a kind of ion chosen from copper, manganese, silver, gold, and rare earth elements at least (1) Or (2) EL material powder of a publication.
- (4) The above whose co-activating agent is a kind of ion chosen from chlorine, a bromine, iodine, and aluminum at least (1) – (3) EL material powder given in either.
- (5) The above whose activator is a copper ion and whose co-activating agent is a chloride ion (1) EL material powder given in either of – (4).

[0007]

[Specific Explanation] The fluorescent substance powder of this invention is fluorescent substance powder of the zinc sulfide base which uses zinc sulfide as a parent and contains the activator (metal ion) and co-activating agent which are an emission center. Although there is two crystal form, the hexagonal system (wurtzite mold beta-ZnS) of an elevated-temperature stability mold (1024 degrees C or more) and the cubic system (sphalerite mold alpha-ZnS) of a low-temperature stability mold, in zinc sulfide, the thing of which crystal form is sufficient as the zinc sulfide used as a parent of fluorescent substance powder in this invention, and both may be intermingled.

[0008] As for the activator used as an emission center, the metal ion generally used to a fluorescent substance is used as an activator. Specifically, copper, manganese, silver, gold, rare earth elements, etc. are used suitably. These may be used independently or may be used combining plurality. It depends for the wavelength region (color) of firefly luminescence on the class of activator, for example, fluorescence, such as green (copper), Orange (manganese), and blue (silver), is acquired. Although the optimal activation agent concentration changes with classes of activator, if luminescence sufficient at less than 0.01% is not obtained that what is necessary is just 0.01 – 0.1% of the weight (following %) of the range but 0.1% is exceeded to the zinc sulfide of a parent, in the case of a copper activator, lowering of brightness will be caused, for example. As co-activating agent, various kinds of co-activating agent currently used for the fluorescent substance is used conventionally. Specifically, chlorine, a bromine, iodine, and aluminum are used suitably. These may be used independently and may be used combining plurality. In the case of chlorine, co-activating agent concentration should just be 0.01 – 0.2% of range to zinc sulfide in a parent. Luminescence sufficient at less than 0.01% is not obtained, but lowering of brightness will be caused if it exceeds 0.2%.

[0009] The field-like stacking fault has arisen to the whole parent of zinc sulfide at homogeneity and high density, and the fluorescent substance powder of this invention is characterized by the average spacing being 0.2–10nm, as shown in the microphotography of drawing 1. Drawing 1 is the example which doped copper sulfide as an activator to zinc sulfide, in this drawing, a substrate part is zinc sulfide of a parent and a stripes-like part is a part of the stacking fault. Drawing 1 shows the cross section of a right angle mostly to the stacking fault which spreads in the shape of a field. Copper sulfide deposits in accordance with the stacking fault of the zinc sulfide of a parent. The fluorescent substance powder of this invention has the very narrow average spacing of each stacking fault so that it may illustrate. The stacking fault of such high density of a spacing can be formed by applying impulse force to medium fluorescent substance powder. Furthermore, the whole particle can be made to distribute an activator deposit part to homogeneity by re-calcinating the fluorescent substance powder which has the stacking fault of this high density. On the other hand, since the most is depositing the activator using the stacking fault which exists in medium fluorescent substance powder automatically, as shown in drawing 2, the average spacing of a stacking fault

is large [ the conventional EL material powder ] compared with the fluorescent substance powder of this invention. it is about  $1/10$  of the in general conventional fluorescent substance powder, and the average spacing between stacking faults in the fluorescent substance powder of this invention is boiled markedly, and its consistency of a stacking fault is high, and is distributing it to the whole parent particle at homogeneity.

[0010] The general process of fluorescent substance powder calcinates the zinc sulfide powder of a raw material primarily with the halogenide used as the metallic compounds used as an activator, and co-activating agent etc., manufactures medium fluorescent substance powder, and deposits an activator focusing on a stacking fault by carrying out secondary baking (re-baking) of this using the stacking fault of the edge dislocation which exists in the interior of the crystal of this medium fluorescent substance powder, twin crystal, etc. This stacking fault is a field-like lattice defect, and an activator deposits in accordance with the stacking fault of the shape of this field in the zinc sulfide crystal of a parent.

[0011] As for zinc sulfide, two crystal form, cubic system ( $\alpha$ -ZnS ) and hexagonal system ( $\beta$ -ZnS ), exists, and, specifically, the maximum dense atomic plane (111) (field) is ABCABC at the former.... The maximum dense atomic plane vertical to c axis in nothing and the latter is ABAB about three layer systems.. The two-layer structure is formed. For this reason, for example, when impulse force is applied to a zinc sulfide crystal, it is  $\alpha$ -ZnS. When the skid of the maximum dense atomic plane happens and C side falls out, it is  $\beta$ -ZnS of ABAB selectively. It becomes and edge dislocation arises, and AB side may be reversed and twin crystal may arise. Generally, in order to concentrate the impurity under crystal on a lattice defect part, if the zinc sulfide which has a stacking fault is heated and activators, such as copper sulfide, are diffused, an activator deposits in a stacking fault. Since the interface of the deposit part of an activator and the zinc sulfide part of a parent takes the lead in EL luminescence, it is advantageous that the consistency of a stacking fault is high, when raising luminescence brightness.

[0012] With the fluorescent substance powder of this invention, since the stacking-fault part into which the activator used as an emission center deposits is distributed over homogeneity over the whole zinc sulfide crystal of a parent as mentioned above and exists in high density, high luminescence brightness is obtained. Moreover, although the luminescence life of EL material powder is lost for the back-diffusion of gas of an activator happening, since the activator is distributed over the whole particle at homogeneity, the deposit consistency of an activator is high and the back-diffusion of gas of an activator itself is controlled that there is little effect of brightness lowering, a luminescence life is long [ the fluorescent substance powder of this invention ].

[0013] The EL material powder of this invention manufactures medium fluorescent substance powder according to a conventional method, it applies impulse force to this, makes the stacking fault of high density produce, is re-calcinated after an appropriate time, deposits an activator in a stacking fault, and manufactures it through surface etching and a surface classification if needed. Medium fluorescent substance powder is obtained by carrying out washing clearance of the fusing agent, and drying, after mixing the metallic compounds and the fusing agent used as an activator to the zinc sulfide powder of a high grade and calcinating primarily at 1000–1300 degrees C. As for the metallic compounds used as an activator, acetate, such as copper, manganese, silver, gold, and rare earth elements, a sulfate, etc. are used. A fusing agent serves as a supply source of co-activating agent at the same time it performs crystal growth of a zinc sulfide parent. As an example of a fusing agent, the halogenide and \*\* of alkali or alkaline earth metal are mentioned.

[0014] Since the narrow activator deposit part of a spacing produces a stacking fault, it applies impulse force to the powder particle of a medium fluorescent substance, and, thereby, makes the whole crystal generate a stacking fault in high density with the fluorescent substance powder of this invention. For example, the powder particle of a medium fluorescent substance is made to collide with a wall at high speed, or particles are made to specifically collide. Re-baking for depositing an activator in a stacking fault is performed by heating at 700–900 degrees C for 2 to 10 hours. Etching removes the zinc-oxide film on the front face of a particle after re-baking. Under the present circumstances, since the copper in a particle may dissolve and it may deposit on a front face, this is preferably removed using EDTA etc. and the EL material powder of the particle size made into the object is obtained through rinsing, desiccation, and a classification.

[0015] The particle size of fluorescent substance powder is 25 micrometers. The following is desirable. Luminescence brightness is influenced also with particle size and its one where particle size is smaller is advantageous. The particle size of fluorescent substance powder is 40 micrometers. Since luminescence

brightness will fall substantially if it becomes above, it is not desirable. Although particle size will become small if the particle size of fluorescent substance powder becomes settled by primary baking which mainly manufactures medium fluorescent substance powder, burning temperature is generally lowered and the amount of fusing agents is reduced. With the conventional fluorescent substance powder, since the balance of the amount of dopes of an activator and co-activating agent will collapse if burning temperature and the amount of fusing agents are lowered, luminescence brightness does not necessarily improve, but a color tone also changes, but since the activator is distributed over the whole particle in the fluorescent substance of this invention at homogeneity at high density, such a fault is not produced in it.

[0016]

[Example]

It is a 2.0g copper acetate hydrate in 150g (impurity metallic element content <0.1ppm) of example 1 high-grade zinc sulfide powder.  $\text{Cu}(\text{CH}_3\text{COO})_2$  and  $\text{H}_2\text{O}$  It adds. As a fusing agent, furthermore, 10g magnesium chloride  $\text{MgCl}_2$  and  $6\text{H}_2\text{O}$ , 5g barium chloride  $\text{BaCl}_2$  and  $2\text{H}_2\text{O}$  And what mixed 10g ammonium-chloride  $\text{NH}_4\text{Cl}$  could be inserted in the container with 150g of nylon balls containing an iron core, and could be rotated for 30 minutes, and it mixed. Subsequently, after enclosing these raw material fine particles with the porcelain crucible and calcinating at 1200 degrees C for 6 hours, 3l. of ion exchange water washed 10 times, - filtration was repeated, the fusing agent was flushed thoroughly, it dried and medium fluorescent substance powder (mean particle diameter of 28 micrometers) was obtained. Next, it is this medium fluorescent substance powder 150 m/sec Impulse force was applied by the approach of making it distributing in a high-speed flow, and making it colliding with a wall surface. In order to avoid mixing of an impurity, the collision wall used what covered the front face with silicone rubber. After applying impulse force, medium fluorescent substance powder is re-calcinated at 700 degrees C for 6 hours, and it agitates for 30 minutes in 5% hydrochloric-acid water solution, and surface etching processing is carried out and classified [rinse, dry and ], and it is the mean particle diameter of 23 micrometers. EL material powder was obtained. The transmission electron microscope image of this fluorescent substance powder is shown in drawing 1. A thin striped pattern is a stacking fault (mainly twin plane), and is distributed over the whole zinc sulfide particle of a parent at homogeneity. A mutual average spacing is 2.5nm. Furthermore, the below-mentioned luminescence characteristic test was performed about this fluorescent substance powder.

[0017] Except having changed example 2 burning temperature and impulse force, EL material powder is manufactured like an example 1, and it is the mean particle diameter of 35 micrometers. EL material powder was obtained. Moreover, the luminescence characteristic test same about this fluorescent substance powder as an example 1 was performed.

[0018] After manufacturing medium fluorescent substance powder by the completely same approach as example of comparison 1 example 1, it re-calcinated, without applying impulse force, and fluorescent substance powder was manufactured. Then, baking conditions, the surface treatment approach, etc. were altogether processed on the same conditions as an example 1, and fluorescent substance powder was obtained. The transmission electron microscope image of this fluorescent substance powder was shown in drawing 2. A thin striped pattern is a stacking fault like drawing 1, and a mutual average spacing is 26nm. Compared with the fluorescent substance powder of an example 1, the average spacing of a stacking fault is large about about 10 times. Furthermore, the luminescence characteristic test same about this fluorescent substance powder as an example 1 was performed.

[0019] EL material powder was manufactured like the example 1 of a comparison except having made example of comparison 2 burning temperature the same as that of an example 2. The luminescence characteristic test same about this fluorescent substance powder as an example 1 was performed.

[0020] About the fluorescent substance powder obtained in the luminescence characteristic test example and the example of a comparison of fluorescent substance powder, mixed each 0.6g of fluorescent substance powder and 0.3g of castor oil, made it the shape of a paste, applied to glass with the electric conduction film, the insulating spacer with a thickness of 100 micrometers was made to be placed between these, and EL light emitting device was produced for the glass with the electric conduction film of one more sheet in piles. The alternating voltage of 120V and 1 kHz was impressed to this light emitting device at the room temperature, and each brightness was measured. The relative luminance and the relative luminance reduction-by-half life in each light emitting device were shown in a table 1. In addition, relative luminance and a reduction-by-half life set to 1 the brightness and brightness reduction-by-half life of a light emitting device which used the fluorescent substance powder of the example 1 of a comparison.

[0021]

[A table 1]

No.	Activator	Co-activating agent	Mean particle diameter	crystal defect	Relative luminance	The brightness reduction-by-half life
example 1	Cu	Cl	23 micrometers	2.5nm	11.20	2.11 **
2	Cu	Cl	35 micrometers	2.7nm	9.35	1.90
Example 1 of comparison	Cu	Cl	24 micrometers	26 nm	1.00	1.00 **
2	Cu	Cl	38 micrometers	30 nm	0.81	1.23

A (notes) crystal defect is the average spacing [0022] of a stacking fault.

[Effect of the Invention] luminescence brightness and a luminescence life are boiling the EL material powder of this invention markedly, and are improving, and the broad utilization to a flat-surface mold display, the luminescence panel for a display, etc. is more possible for it than the conventional EL material powder.

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**DESCRIPTION OF DRAWINGS**

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**[Brief Description of the Drawings]**

**[Drawing 1]** The transmission electron microscope photograph showing the organization condition of the fluorescent substance particle concerning this invention.

**[Drawing 2]** The transmission electron microscope photograph showing the organization condition of the fluorescent substance particle concerning the example of a comparison.

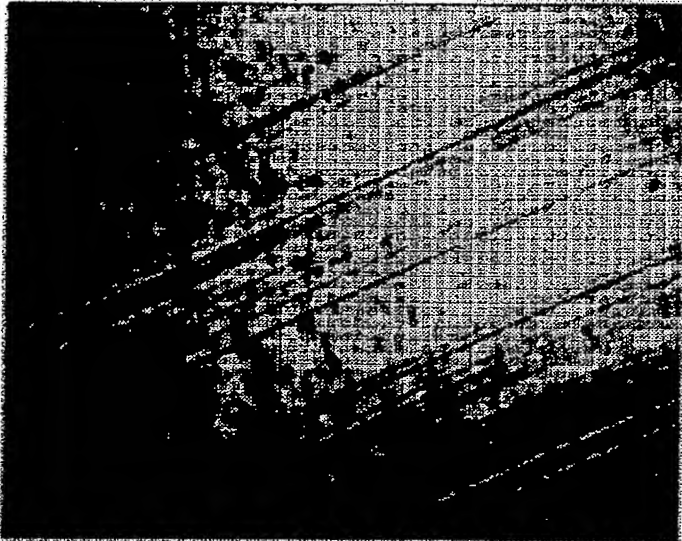
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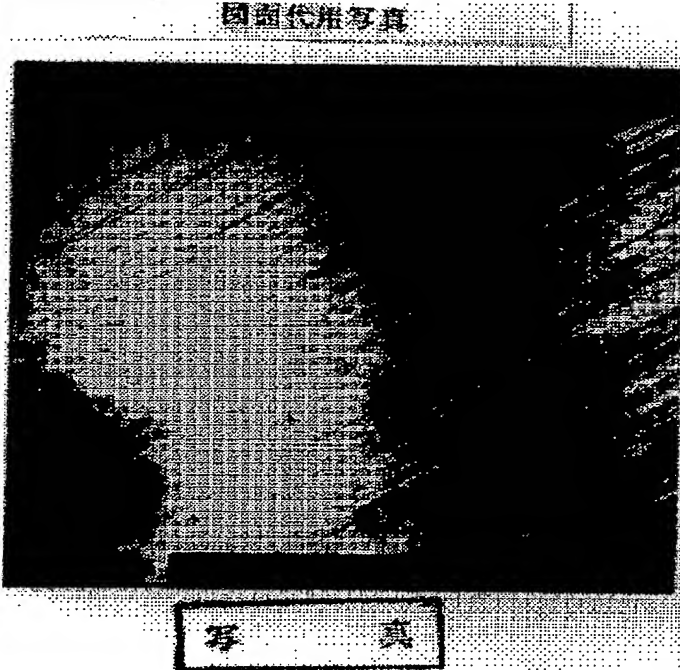
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DRAWINGS

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[Drawing 1]



[Drawing 2]

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(54) 【発明の名称】 E L 蛍光体粉末

(57) 【要約】

【構成】 硫化亜鉛を母体とし付活剤および共付活剤を含有する蛍光体粉末であって、積層欠陥を粒子全体に均一かつ高密度に有しており、その積層欠陥の平均面間隔が0.2~10nmであり、好ましくは平均粒径が25μm以下のエレクトロルミネッセンス (E L) 蛍光体粉末。

【効果】 従来のE L 蛍光体粉末よりも発光輝度および発光寿命が格段に向上しており、平面型ディスプレイや表示用発光パネルなどへの幅広い利用が可能である。

## 【特許請求の範囲】

【請求項1】 硫化亜鉛を母体とし付活剤および共付活剤を含有する蛍光体粉末であって、面状の積層欠陥を粒子全体に均一かつ高密度に有しており、その積層欠陥の平均面間隔が0.2～10nmであることを特徴とするエレクトロルミネッセンス(EL)蛍光体粉末。

【請求項2】 蛍光体粉末の平均粒径が25 $\mu\text{m}$ 以下の請求項1のEL蛍光体粉末。

【請求項3】 付活剤が銅、マンガン、銀、金および希土類元素から選択された少なくとも一種のイオンである請求項1または2のEL蛍光体粉末。

【請求項4】 共付活剤が塩素、臭素、ヨウ素およびアルミニウムから選択された少なくとも一種のイオンである請求項1～3のいずれかに記載のEL蛍光体粉末。

【請求項5】 付活剤が銅イオンであり、共付活剤が塩素イオンである請求項1～4のいずれかに記載のEL蛍光体粉末。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は、硫化亜鉛を母体とし発光の中心となる付活剤および共付活剤を含有する蛍光体粉末、特に、高輝度で長寿命のエレクトロルミネッセンス(EL)蛍光体に関する。

## 【0002】

【従来技術】 EL蛍光体は電圧励起型の蛍光体であり、蛍光体粉末を電極の間に挟んで発光素子とした分散型ELと薄膜型ELとが知られている。分散型EL蛍光体の一般的な形状は、蛍光体粉末を高誘電率のバインダー中に分散したものを、少なくとも一方が透明な二枚の電極の間に挟み込んだ構造からなり、両電極間に交流電場を印加することにより発光する。EL蛍光体粉末を用いて作成された発光素子は数mm以下の厚さとすることが可能で、面発光体であり、発熱がなく発光効率が良いなど数多くの利点を有するため、道路標識等の表示用発光パネル、各種インテリアやエクステリア用の照明、液晶ディスプレイ等のフラットパネルディスプレイ用の光源等としての用途が期待されている。

【0003】 EL蛍光体粉末としては、硫化亜鉛を母体として、銅等の付活剤(発光中心としての金属イオン)および塩素等の共付活剤が添加されたものが広く知られている。しかし、この蛍光体粉末を用いて作成された発光素子は、他の原理に基づく発光素子と比べて発光輝度が低く、また発光寿命が短いという欠点があり、このため従来から種々の改良が試みられてきた。例えば、特開昭61-296085号には、硫化亜鉛、銅化合物、ハロゲン化合物の混合物を1000～1200℃で焼成することにより六方晶系の中間蛍光体粉末を製造し、これに常温下で静水圧を加えた後に700～950℃でアニールするか、またはアニールと同時に熱間プレスして立方晶系に転移させ、高輝度、長寿命の蛍光体粉末を製造す

る方法が記載されている。また、特開平6-33053号には、中間蛍光体粉末を大気中でアニールする方法に代えて、硫酸塩存在下で大気を遮断して再焼成し、エッチング後さらに大気中で比較的低温で熱処理する製造方法が記載されている。後者の方法で製造された蛍光体粉末は従来のものより発光輝度が高く、寿命も長い利点を有しているが、さらに、その高輝度化および長寿命化が求められている。

## 【0004】

【発明の解決課題】 本発明は、従来のEL蛍光体粉末における上記課題を解決したものであって、発光素子用として十分な高輝度、長寿命特性を有するEL蛍光体粉末を提供することを目的とする。

## 【0005】

【課題の解決手段】 EL蛍光体粉末のEL発光の中心は、粒子内に存在する積層欠陥部に析出した付活剤の硫化銅( $\text{Cu}_2\text{S}$ )等の針状結晶と硫化亜鉛母体との界面部分であると考えられている(『銅付活蛍光体』セラミックス26(1991) No.7)。本発明者等は従来のEL蛍光体粉末が、粒子内に自然に存在する積層欠陥を利用しているためEL発光の中心となる積層欠陥の密度が低く、従って高輝度発光を得られないことを見出した。そこで本発明においては、中間蛍光体粉末に衝撃力を加えるなどの方法により面状の積層欠陥を粒子全体に均一かつ高密度に生じさせ、EL発光の中心部分を硫化亜鉛粒子全体に均一に分散させ、その密度を高めることにより発光輝度と発光寿命を大幅に向上させた。

【0006】 すなわち、本発明によれば、以下の構成を有するEL蛍光体粉末とその製造方法が提供される。

(1) 硫化亜鉛を母体とし付活剤および共付活剤を含有する蛍光体粉末であって、面状の積層欠陥を粒子全体に均一かつ高密度に有しており、その積層欠陥の平均面間隔が0.2～10nmであることを特徴とするEL蛍光体粉末。

(2) 蛍光体粉末の平均粒径が25 $\mu\text{m}$ 以下の上記(1)のEL蛍光体粉末。

(3) 付活剤が銅、マンガン、銀、金および希土類元素から選択された少なくとも一種のイオンである上記(1)または(2)に記載のEL蛍光体粉末。

(4) 共付活剤が塩素、臭素、ヨウ素およびアルミニウムから選択された少なくとも一種のイオンである上記(1)～(3)のいずれかに記載のEL蛍光体粉末。

(5) 付活剤が銅イオンであり、共付活剤が塩素イオンである上記(1)～(4)のいずれかに記載のEL蛍光体粉末。

## 【0007】

【具体的な説明】 本発明の蛍光体粉末は、硫化亜鉛を母体とし、発光中心である付活剤(金属イオン)および共付活剤を含有する硫化亜鉛ベースの蛍光体粉末である。硫化亜鉛には高温安定型(1024℃以上)の六方晶系(ウ

ルツ鉱型  $\beta$ -ZnS) と低温安定型の立方晶系 (閃亜鉛鉱型  $\alpha$ -ZnS) の2つの結晶形があるが、本発明において蛍光体粉末の母体として用いる硫化亜鉛はいずれの結晶形のもでもよく、両者が混在していてもよい。

【0008】 蛍光中心となる付活剤は、付活剤として蛍光体に一般に使用される金属イオンが用いられる。具体的には、銅、マンガ、銀、金および希土類元素等が好適に用いられる。これらは単独で用いても、複数を組み合わせて用いてもよい。蛍光発光の波長域 (色) は付活剤の種類に依存しており、例えば、緑色 (銅)、オレンジ (マンガ)、青 (銀) 等の蛍光が得られる。最適付活剤濃度は付活剤の種類により異なるが、たとえば、銅付活剤の場合は母体の硫化亜鉛に対して0.01~0.1重量% (以下%) の範囲であればよく、0.01%未満では十分な発光が得られず、0.1%を越えると輝度の低下を招く。共付活剤としては、従来、蛍光体に使用されている各種の共付活剤が用いられる。具体的には塩素、臭素、ヨウ素およびアルミニウムが好適に用いられる。これらは単独で用いてもよく、複数を組み合わせて用いてもよい。共付活剤濃度は塩素の場合、母体中で硫化亜鉛に対し0.01~0.2%の範囲であればよい。0.01%未満では十分な発光が得られず、0.2%を越えると輝度の低下を招く。

【0009】 本発明の蛍光体粉末は、図1の顕微鏡写真に示すように、面状の積層欠陥が硫化亜鉛の母体全体に均一かつ高密度に生じており、その平均面間隔が0.2~10nmであることを特徴とする。図1は硫化亜鉛に付活剤として硫化銅をドーブした例であり、同図において基質部分は母体の硫化亜鉛であり、縞状の部分はその積層欠陥の部分である。図1は面状に広がる積層欠陥に対してほぼ直角の断面を示している。硫化銅は母体の硫化亜鉛の積層欠陥に沿って析出する。図示するように本発明の蛍光体粉末は、各積層欠陥の平均面間隔が極めて狭い。このような面間隔の高密度の積層欠陥は、中間蛍光体粉末に衝撃力を加えることにより形成することができる。さらに、この高密度の積層欠陥を有する蛍光体粉末を再焼成することにより付活剤析出部分を粒子全体に均一分散させることができる。一方、従来のEL蛍光体粉末は、その大部分が中間蛍光体粉末に自然に存在する積層欠陥を利用して付活剤を析出させているため、図2に示すように、積層欠陥の平均面間隔が本発明の蛍光体粉末に比べて広い。本発明の蛍光体粉末における積層欠陥相互の平均面間隔は、概ね、従来の蛍光体粉末の約10分の1であり、積層欠陥の密度が格段に高く、かつ母体粒子全体に均一分散している。

【0010】 蛍光体粉末の一般的な製法は、原料の硫化亜鉛粉末を付活剤となる金属化合物および共付活剤となるハロゲン化物などと共に一次焼成して中間蛍光体粉末を製造し、この中間蛍光体粉末の結晶内部に存在する刃状転位や双晶などの積層欠陥を利用して、これを二次焼

成 (再焼成) することにより積層欠陥を中心に付活剤を析出させる。この積層欠陥は面状の格子欠陥であり、母体の硫化亜鉛結晶内において、この面状の積層欠陥に沿って付活剤が析出する。

【0011】 具体的には、硫化亜鉛は立方晶系 ( $\alpha$ -ZnS) と六方晶系 ( $\beta$ -ZnS) の2つの結晶形が存在し、前者では最密原子面 (111) 面はABCABC……の三層構造をなし、後者ではc軸に垂直な最密原子面がABAB……の二層構造を形成している。このため、例えば、硫化亜鉛結晶に衝撃力を加えた場合、 $\alpha$ -ZnSで最密原子面のすべりが起こりC面が抜けると部分的にABABの $\beta$ -ZnSとなり刃状転位が生じ、また、AB面が逆転して双晶が生じることもある。一般に、結晶中の不純物は格子欠陥部分に集中するため、積層欠陥を有する硫化亜鉛を加熱して硫化銅などの付活剤を拡散させると積層欠陥に付活剤が析出する。付活剤の析出部分と母体の硫化亜鉛部分との界面がEL発光の中心となることから、積層欠陥の密度が高いことは発光輝度を高めるうえで有利である。

【0012】 本発明の蛍光体粉末では、発光中心となる付活剤が析出する積層欠陥部分が前述のように母体の硫化亜鉛結晶全体にわたって均一に分布し、かつ高密度に存在するために高い発光輝度が得られる。また、EL蛍光体粉末の発光寿命が失われるのは付活剤の逆拡散が起こるためであるが、本発明の蛍光体粉末は、付活剤が粒子全体に均一に分布しているため輝度低下の影響が少なく、また付活剤の析出密度が高いために付活剤の逆拡散自体が抑制されるので発光寿命が長い。

【0013】 本発明のEL蛍光体粉末は、常法に従い中間蛍光体粉末を製造し、これに衝撃力を加えて高密度の積層欠陥を生ぜしめ、しかる後に再焼成して付活剤を積層欠陥内に析出させ、必要に応じ、表面のエッチングおよび分級を経て製造する。中間蛍光体粉末は、高純度の硫化亜鉛粉末に付活剤となる金属化合物および融剤を混合し、1000~1300℃で一次焼成した後、融剤を洗浄除去し乾燥することにより得られる。付活剤となる金属化合物は銅、マンガ、銀、金および希土類元素等の酢酸塩、硫酸塩等が用いられる。融剤は硫化亜鉛母体の結晶成長を行うと同時に、共付活剤の供給源となる。融剤の例としては、アルカリやアルカリ土類金属のハロゲン化物および等が挙げられる。

【0014】 本発明の蛍光体粉末では、面間隔の狭い付活剤析出部分は積層欠陥を生じさせるために、中間蛍光体の粉末粒子に衝撃力を加え、これにより結晶全体に積層欠陥を高密度に発生させる。例えば、具体的には、中間蛍光体の粉末粒子を高速で壁に衝突させ、または粒子どうしを衝突させる。付活剤を積層欠陥内に析出させるための再焼成は、例えば、700~900℃で2~10時間加熱することにより行なわれる。再焼成後、エッチングにより粒子表面の酸化亜鉛膜を除去する。この際、

粒子中の銅が溶解して表面に析出することがあるため、これを好ましくはEDTAなどを用いて除き、水洗、乾燥、分級を経て、目的とする粒径のEL蛍光体粉末を得る。

【0015】蛍光体粉末の粒径は25 $\mu\text{m}$ 以下が好ましい。発光輝度は粒径によっても影響を受け、粒径が小さいほうが有利である。蛍光体粉末の粒径が40 $\mu\text{m}$ 以上になると発光輝度が大幅に低下するので好ましくない。蛍光体粉末の粒径は主に中間蛍光体粉末を製造する一次焼成によって定まり、一般に焼成温度を下げて融剤量を減らせば粒径は小さくなるが、従来の蛍光体粉末では焼成温度や融剤量を下げると付活剤および共付活剤のドーブ量のバランスが崩れるために発光輝度は必ずしも向上せず、色調も変化するが、本発明の蛍光体では付活剤が高密度に粒子全体に均一に分布しているのでこのような欠点を生じない。

【0016】

【実施例】

実施例1

高純度硫化亜鉛粉末（不純物金属元素含有量<0.1ppm）150gに2.0gの酢酸銅水和物 $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ を加え、さらに、融剤として10gの塩化マグネシウム $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 、5gの塩化バリウム $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ および10gの塩化アンモニウム $\text{NH}_4\text{Cl}$ を混合したものを、鉄心入りナイロン球150gと共に容器に装入し、30分間回転させてよく混合した。次いで、この原料粉末を磁製ルツボに封入し、1200℃で6時間焼成した後、イオン交換水3リットルで10回洗浄し・濾過を繰り返して融剤を完全に洗い流し、乾燥して中間蛍光体粉末（平均粒径28 $\mu\text{m}$ ）を得た。次に、この中間蛍光体粉末を150m/secの高速気流中に分散させて壁面に衝突させる方法によって衝撃力を加えた。不純物の混入を避けるため、衝突壁は表面をシリコンゴムで被覆したものをを用いた。衝撃力を加えた後、中間蛍光体粉末を700℃で6時間再焼成し、5%塩酸水溶液中で30分間攪拌して表面エッチング処理を行ない、水洗、乾燥、分級して、平均粒径23 $\mu\text{m}$ のEL蛍光体粉末を得た。この\*

\*蛍光体粉末の透過電子顕微鏡像を図1に示す。細い縞模様は積層欠陥（主として双晶面）であり、母体の硫化亜鉛粒子全体に均一に分布している。相互の平均面間隔は2.5nmである。さらに、この蛍光体粉末について後述の発光特性試験を行った。

【0017】実施例2

焼成温度、衝撃力を変えた以外は実施例1と同様にしてEL蛍光体粉末を製造し、平均粒径35 $\mu\text{m}$ のEL蛍光体粉末を得た。またこの蛍光体粉末について実施例1と同様の発光特性試験を行った。

【0018】比較例1

実施例1と全く同様の方法で中間蛍光体粉末を製造した後に、衝撃力を加えずに再焼成して蛍光体粉末を製造した。その後、焼成条件および表面処理方法など全て実施例1と同一の条件で処理し蛍光体粉末を得た。この蛍光体粉末の透過電子顕微鏡像を図2に示した。図1と同様に細い縞模様は積層欠陥であり、相互の平均面間隔は26nmである。実施例1の蛍光体粉末に比べて積層欠陥の平均面間隔は約10倍程度大きい。さらに、この蛍光体粉末について実施例1と同様の発光特性試験を行った。

【0019】比較例2

焼成温度を実施例2と同一とした以外は、比較例1と同様にしてEL蛍光体粉末を製造した。この蛍光体粉末について実施例1と同様の発光特性試験を行った。

【0020】蛍光体粉末の発光特性試験

実施例および比較例で得た蛍光体粉末について、各々の蛍光体粉末0.6gとひまし油0.3gを混合しペースト状にして導電膜付きガラスに塗布し、これに厚さ100 $\mu\text{m}$ の絶縁スペーサーを介在させて、もう1枚の導電膜付きガラスを重ねてEL発光素子を作製した。この発光素子に室温で120V、1kHzの交流電圧を印加して各々の輝度を測定した。各発光素子における相対輝度および相対輝度半減寿命を表1に示した。なお相対輝度および半減寿命は比較例1の蛍光体粉末を用いた発光素子の輝度および輝度半減寿命を1とした。

【0021】

【表1】

No.	付活剤	共付活剤	平均粒径	結晶欠陥	相対輝度	輝度半減寿命
実施例1	Cu	Cl	23 $\mu\text{m}$	2.5nm	11.20	2.11
" 2	Cu	Cl	35 $\mu\text{m}$	2.7nm	9.35	1.90
比較例1	Cu	Cl	24 $\mu\text{m}$	26nm	1.00	1.00
" 2	Cu	Cl	38 $\mu\text{m}$	30nm	0.81	1.23

（注）結晶欠陥は積層欠陥の平均面間隔

【0022】

【発明の効果】本発明のEL蛍光体粉末は、従来のEL蛍光体粉末よりも発光輝度および発光寿命が格段に向上しており、平面型ディスプレイや表示用発光パネルなどへの幅広い利用が可能である。

【図面の簡単な説明】

【図1】本発明に係る蛍光体粒子の組織状態を表わす透過電子顕微鏡写真。

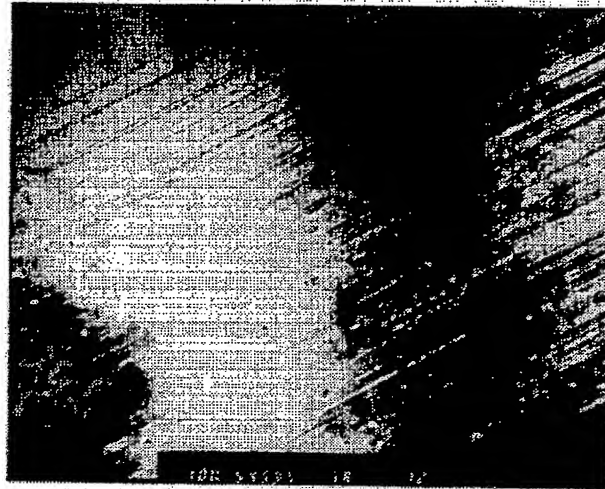
【図2】比較例に係る蛍光体粒子の組織状態を表わす透過電子顕微鏡写真。

(5)

特開平8-183954

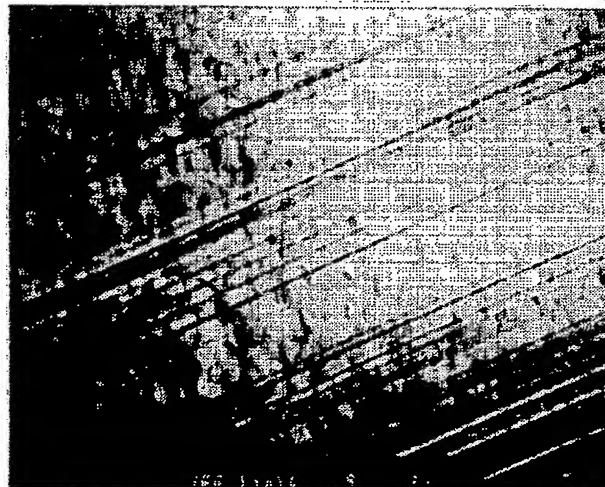
【図1】

図面代用写真



【図2】

図面代用写真



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